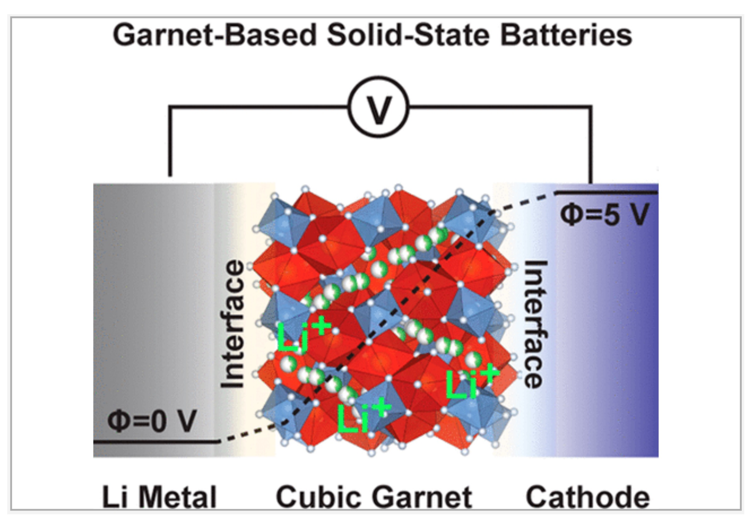
Depositing $Li_{7-x}\,La_3\,Zr_{2-x}\,Ta_xO_{12}$ (LLZTO) Thin Films Using Pulse Laser Deposition

Alkhatab Al Busaidi, Genaro Lozano, Mackenzie Walker, Tina Tong, Sujan Shrestha, and Ambrose Seo
Department of Physics and Astronomy
University of Kentucky

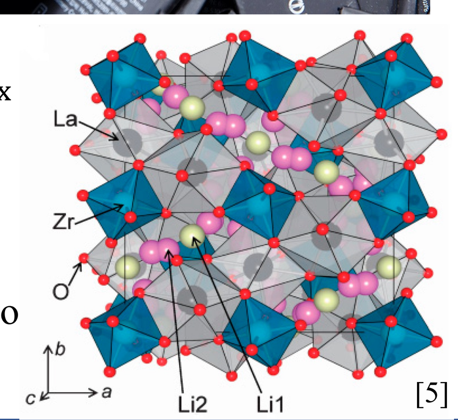
ABSTRACT: Recently, lithium-ion batteries became of a great interest in industry due to their high energy density and reasonable price. Garnet-type electrolytes (e.g., LLZTO) can be of great contribution to these batteries due to their outstanding properties. In this research, LLZTO thin film was deposited using Pulse Laser Deposition (PLD) technique, which is based on physical vapor deposition. An LLZTO pellet (target for PLD) was re-grinded and a new pellet was produced, using uniaxial dry pressing followed by sintering and X-ray Diffraction (XRD) analysis. The LLZTO film was deposited on a stainless-steel substrate at 500 °C for 40 min . The oxygen partial pressure was 75 mTorr with an energy of 452 mJ. The XRD of the target/pellet before PLD was generally good and matched with literature. After the PLD, generally LLZTO was not deposited. However, it is still cannot be concluded that LLZTO was not deposited, as the peaks between angles 40° to 60° match with the original LLZTO target, so it may be that the peaks of stainless-steel and LLZTO on stainless-steel had interfered. However, this needs more investigation and evaluation in order to give a final conclusion.

Background & Motivation

- Lithium-ion batteries (LIB) are considered to have high energy density and reasonable price [1]
- However, current liquid LIBs have the risk of leakage [1] and flammability [2]
- For future solid-state LIBs, LLZTO is one of the candidates
- Garnet-type electrolytes (e.g., LLZTO) are considered to have great energy density, high temperature stability, electrochemical stability and safety [3]
- Thin films have better properties, due to morphology, composition and structure [4]
- Thin films are more applicable and can cover large areas (contact area)



- Lithium lanthanum zirconium tantalum oxide ($Li_{7-x}\,La_3\,Zr_{2-x}\,Ta_xO_{12}$) is modified version of $Li_7La_3Zr_2O_{12}$ (LLZO)
- Ta occupies some of the Zr sites and helps maintaining a cubic structure [3]
- Cubic structure has higher conductivity (can reach to 10^{-4} S/cm at RT) than tetragonal structure [3]



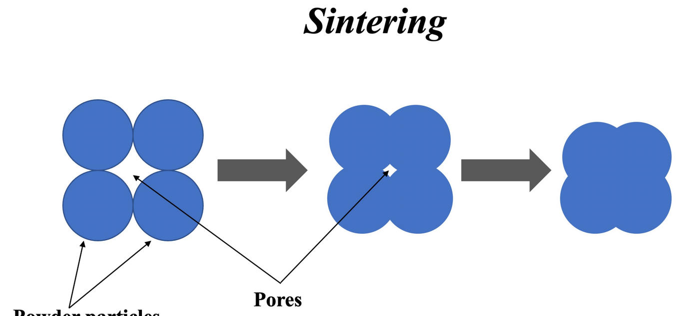
Introduction

Aims:

- To re-synthesize an LLZTO target
- Mainly: Depositing thin films of LLZTO
- Characterizing LLZTO thin film properties

Sintering

- Densification and improving mechanical properties

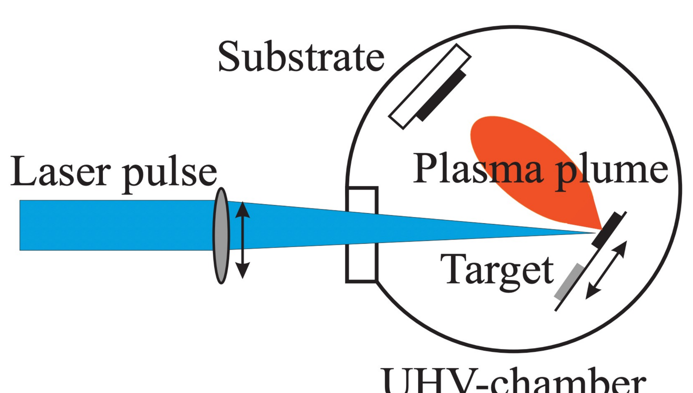


X-ray Diffraction (XRD)

- Used to check the crystal structure, impurities and phases

Pulse Laser Deposition (PLD)

- Based on physical vapor deposition (PVD). In a high-vacuum chamber, a beam of laser strikes the sample. The sample will evaporate as plasma plume and then deposited as a thin film on a substrate [6]



Hypotheses:

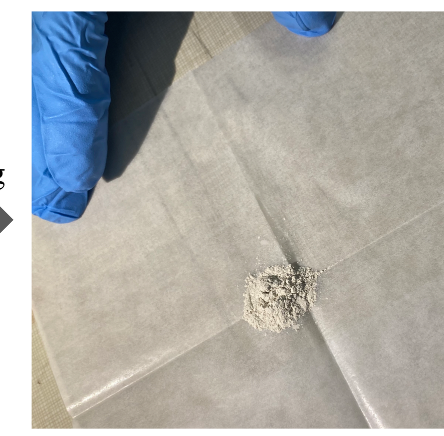
- During re-synthesizing, samples may break
- In general, the deposition may be challenging
- Different substrates need to examined
- High temperatures will cause Li loss, due to Li volatility

Procedures

Commercially purchased LLZTO pellet

Grinding

LLZTO Powder

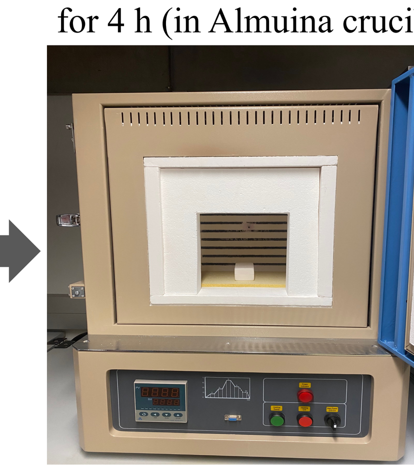


Uniaxial Dry Pressing

- Pressure of 20 Tlb for 60 min

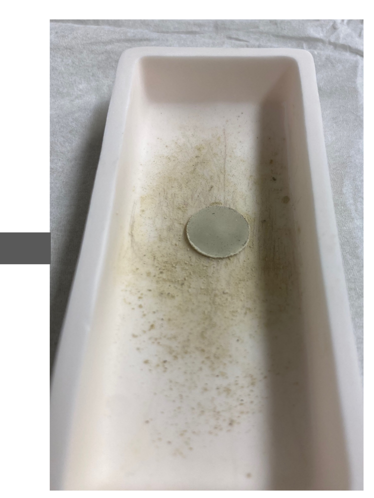
Sintering

- Heated to 600 °C and held there for 4 h (in Almuina crucible



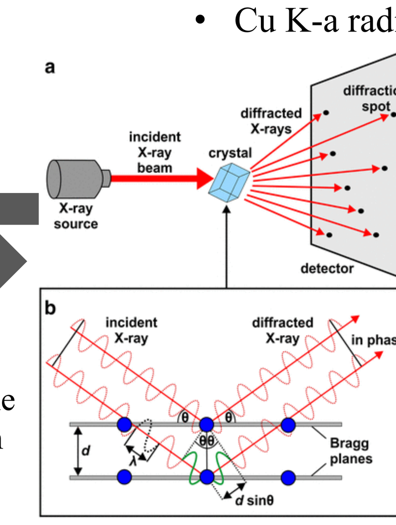
- Pellet was covered with tiny amounts of LLZTO powder (left-over from dry pressing) to compensate for any Li loss during sintering

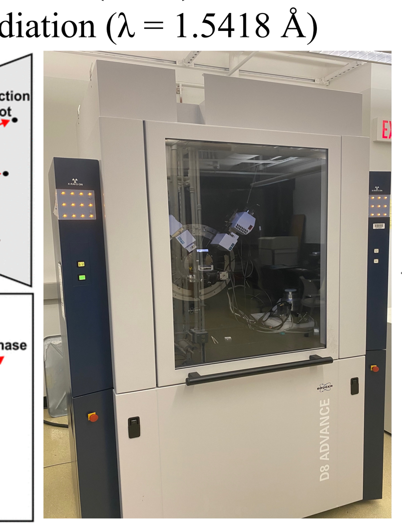
Resultant pellet



X-ray Diffraction (XRD)

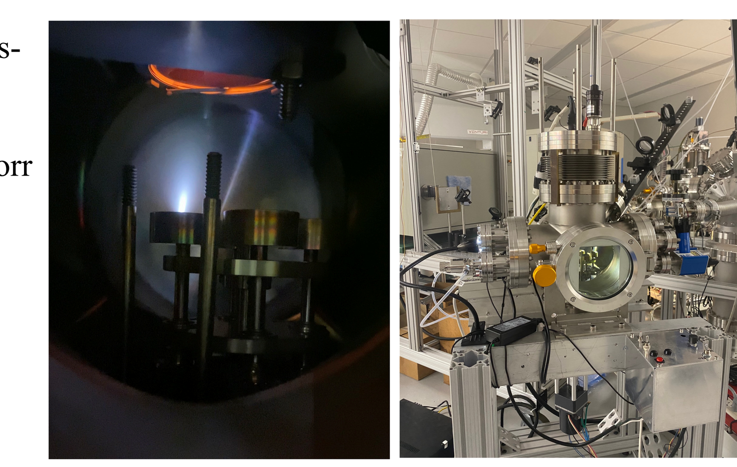
- Cu K-a radiation (λ = 1.5418 Å)





Pulse Laser Deposition (PLD)

- Deposition on stainless-steel substrate
- P_{O2} = 75 mTorr
- $P_{Background}$ = 5.10E-5 Torr
- Temperature = 500 °C
- Energy = 452 mJ

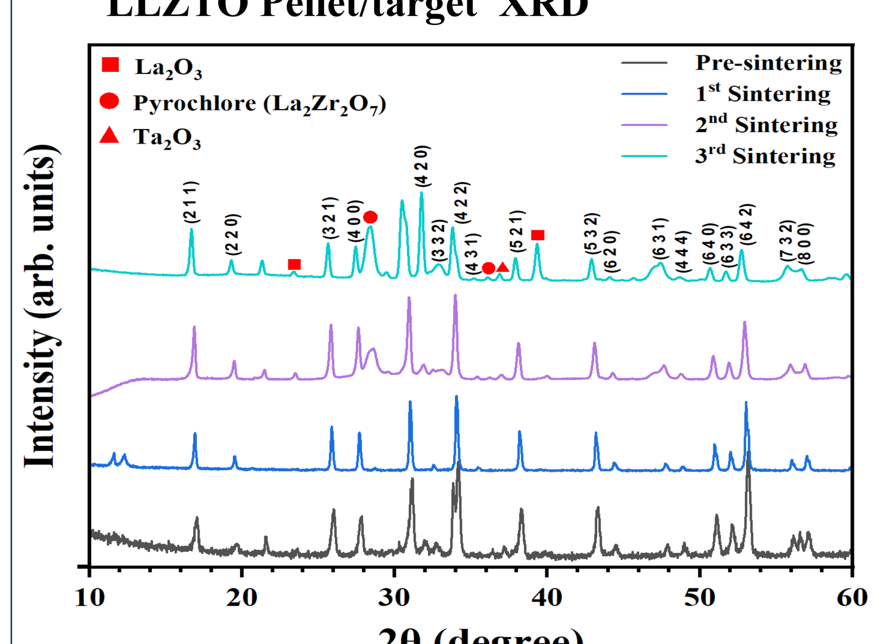


After deposition (XRD for the LLZTO thin film)

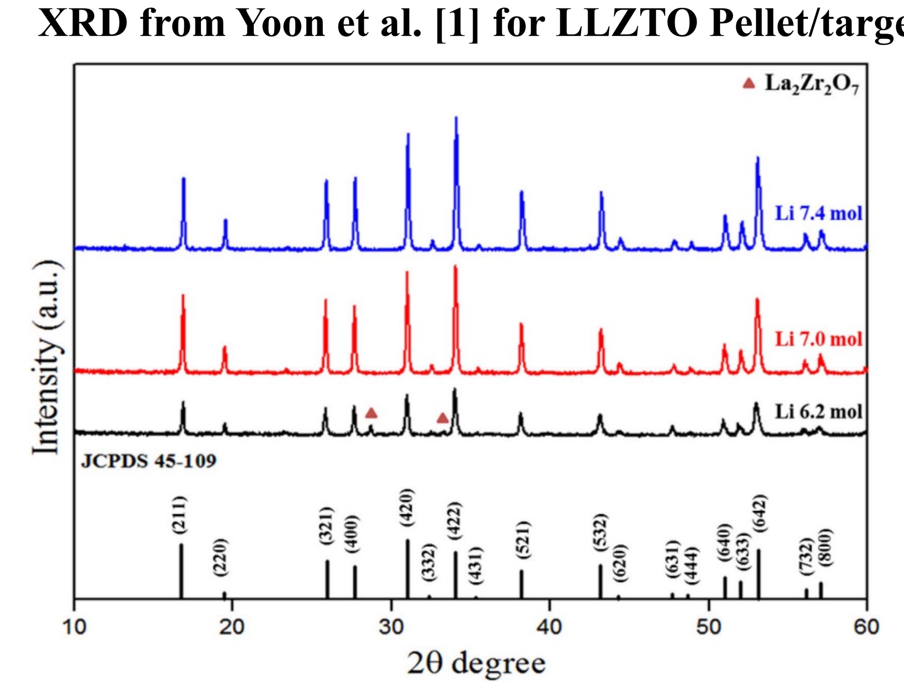
Results and Discussion

X-ray Diffraction (XRD)

LLZTO Pellet/target XRD

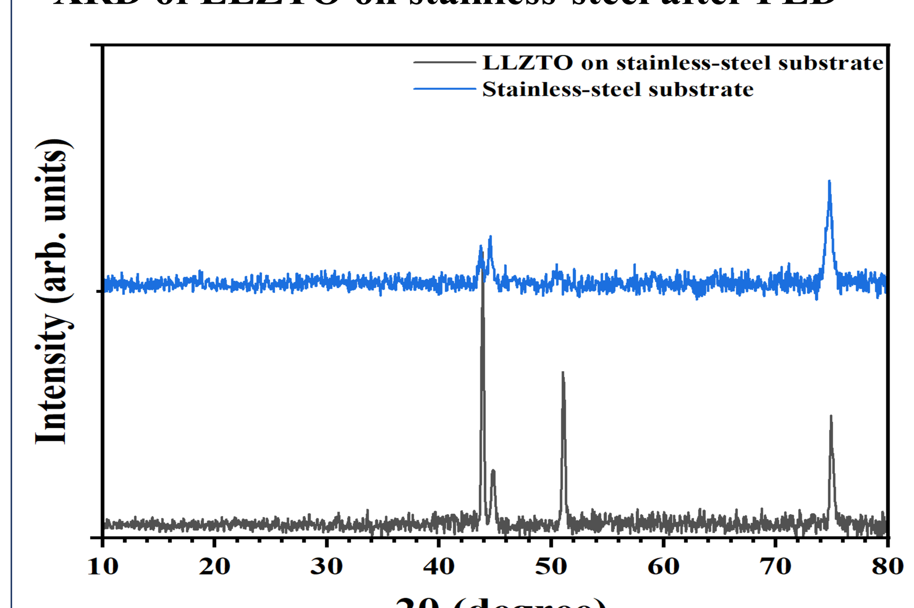


XRD from Yoon et al. [1] for LLZTO Pellet/target

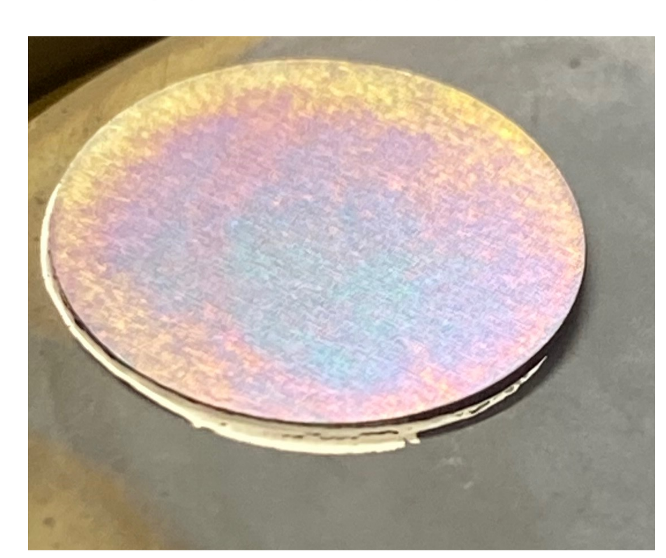


- All Peaks match with some additional peaks, which is quite expected, as the exposure to high temperatures will cause Li loss, due to it volatility.
- 1st sintering almost matched with the Li 7.4 mol, 2nd and 3rd sintering a mostly matched the Li 6.2 mol (expected)
- Shifts and minor shifts between scans can be due to the pellet/sample height difference (as examined)

XRD of LLZTO on stainless-steel after PLD



LLZTO on stainless-steel after PLD



- Generally, the deposition did not work well
- However, the peaks between the angles 40° to 60° almost matched with the original LLZTO target's XRD
- This may be an interference between the stainless-steel substrate's peaks with the deposited LLZTO peaks
- More testing and investigation needs to be done in order get a clear and final conclusion (like X-ray Photoelectron Spectroscopy (XPS) which helps in analyzing the surface)

Conclusions

- As expected, high temperatures results in losing Li, as Li tend to escape the sample due to its high volatility. Therefore, phases may be affected
- The final Li content can be said to be 6.2 mol, based on literature
- The overall LLZTO deposition did not work quite well
- However, there were some peaks between the angles 40° to 60° that almost matched with the original LLZTO target's XRD
- These peaks can also be an interference between the the stainless-steel substrate XRD and the LLZTO XRD, but more investigation needs to be done in order to get better conclusion

Future Work

- Repeat the experiment in order to get more accurate data
- Do more investigation using X-ray Photoelectron Spectroscopy (XPS)
- Examining different substrates, like MgO, Al_2O_3, Cu foil, etc.
- Trying different deposition conditions, manipulating temperature, pressure, deposition period, etc.
- Characterizing the LLZTO thin film and its properties
- Working to deposit epitaxial thin films of LLZTO

References

- [1] Sang A Yoon et al. "Preparation and Characterization of Ta substituted Li 7 La 3 Zr 2-x O 12 Garnet Solid Electrolyte by Sol-Gel Processing". In: Journal of the Korean Ceramic Society 54.4 (2017), pp. 278–284.
- [2] Q. Liu et al., "Challenges and perspectives of garnet solid electrolytes for all solid-state lithium batteries", *Journal of Power Sources*, vol. 389, pp. 120-134, 2018.
- [3] Chengwei Wang et al. "Garnet-type solid-state electrolytes: materials, interfaces, and batteries". In: *Chemical reviews 120.10* (2020), pp. 4257–4300.
- [4] Mattia Saccoccio et al. "Low temperature pulsed laser deposition of garnet Li6. 4La3Zr1. 4Ta0. 6O12 fils as all solid-state lithium battery electrolytes". In: *Journal of Power Sources 365* (2017), pp. 43–52.
- [5] M. Raju, F. Altayran, M. Johnson, D. Wang and Q. Zhang, "Crystal Structure and Preparation of Li7La3Zr2O12 (LLZO) Solid-State Electrolyte and Doping Impacts on the Conductivity: An Overview", *Electrochem*, vol. 2, no. 3, pp. 390-414, 2021.
- [6] Hans-Ulrich Krebs et al. "Pulsed laser deposition (PLD)–a versatile thin film technique". In: *Advances in Solid State Physics* (2003), pp. 505–518.

Acknowledgement

- This work was supported by the National Science Foundation (NSF) Grant No. DMR-2104296 and the Vehicle Technologies Office of the U.S. Department of Energy Battery Materials Research (BMR) Program under Contract Number DD-EE0008863.Also, we thank Prof. William Gannon, Prof. Lance Delong, Santosh Bhusal and Nancy Miller for helping us.